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COMPUTATIONAL INVESTIGATION OF THE STRUCTURES AND RELATIVE
STABILITIES OF AMINO/NITRO DERIVATIVES OF ETHYLENE

by

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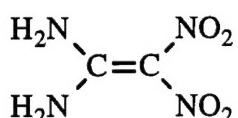
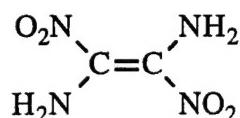
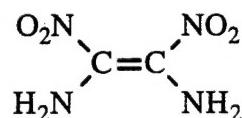
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Abstract

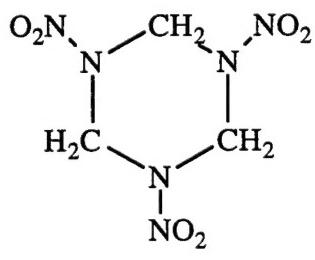
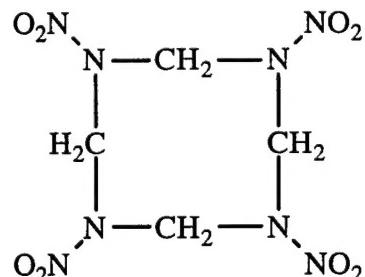
Eight amino and/or nitro derivatives of ethylene have been investigated computationally at the density functional B3P86/6-31+G** level. The molecular geometries and relative stabilities reflect the varying roles of "push-pull" electronic delocalization and intramolecular hydrogen bonding. The same two factors affect, to varying extents, the computed C-NO₂ and C-NH₂ bond dissociation energies, which are also presented, as are the heats of formation, vaporization and sublimation of the three diaminodinitroethylenes. The potential of the latter as energetic compounds is briefly discussed.

1. Introduction

The three isomeric diaminodinitroethylenes, **1** - **3**, are of interest from both theoretical and practical standpoints. They combine the resonance-donating NH₂ and the inductively-withdrawing NO₂ groups in a molecular framework containing polarizable electronic charge. In addition, each molecule presents the opportunity for two or more hydrogen-bonding interactions. The roles played by these factors, electron delocalization and intramolecular hydrogen bonding, can be expected to depend upon the relative positions of the substituents in each isomer.

**1****2****3**

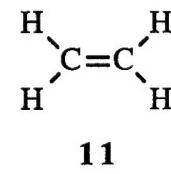
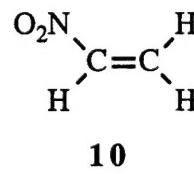
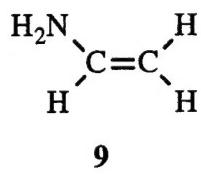
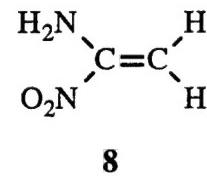
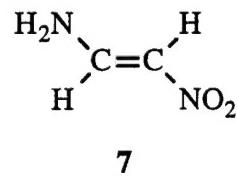
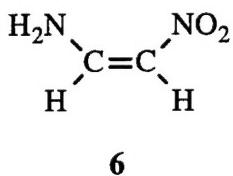
A further interesting feature of **1** - **3** is that they have the same molecular stoichiometry as RDX, **4**, and HMX, **5**, which are among the most effective currently-used explosives and monopropellants [1, 2]. Upon complete decomposition to CO, N₂ and H₂O, all of these molecules, **1** - **5**, would yield the same high value, 0.0405, for moles of gaseous products per gram of compound. Since this ratio is one of the key determinants of explosive and propellant performance, affecting such properties as detonation pressure, detonation velocity and specific impulse [1, 3-5], it follows that the diaminodinitroethylenes merit investigation as potentially-useful energetic molecules, ingredients of explosive and/or propellant formulations.

**4****5**

In the present work, we have used density functional computational techniques to assess the effects of electron delocalization and intramolecular hydrogen bonding in determining the structures and the relative stabilities of **1** - **3**, as well as certain key properties relating to their energetic performance. These include heats of formation and C–NO₂ and C–NH₂ bond dissociation energies.

2. Procedure

All calculations were carried out with a density functional option of the Gaussian 94 code [6]. The Becke three-parameter-hybrid (B3) in conjunction with the Perdew-86 (P86) functional were used to account for exchange/correlation effects [7, 8]. The basis set was the 6-31+G**. Geometry optimizations were carried out for **1 - 3** and for **6 - 11**, and for the dissociation products formed by breaking a single C-NO₂ or C-NH₂ bond in each case. The molecules **6 - 11** were included in order to provide additional perspective and insight into the effects operating in **1 - 3**. The computed energies at 0 K were in all instances converted to enthalpies at 298 K, using the calculated vibrational frequencies [9]. These enthalpies were used to obtain the C-NO₂ and C-NH₂ dissociation energies.



Gas phase heats of formation for **1 - 3** were determined by our density functional procedure that has been described earlier [10, 11]. From these can be obtained the liquid and solid phase values by subtracting, respectively, the heats of vaporization and sublimation. These were estimated by means of relationships that we have developed involving the computed electrostatic potentials and the areas of the molecular surfaces [12, 13].

3. Results

Figure 1 and Table 1 summarize the optimized bond lengths, energies at 0 K and enthalpies at 298 K of **1 - 3** and **6 - 11**. The relative stabilities within the groups **1 - 3** and **6 - 8** are in Table 2. The calculated C-NO₂ and C-NH₂ dissociation energies are given in Tables 3 and 4, and our heats of formation for **1 - 3** (gas, liquid and solid phase) are in Table 5, along with the estimated heats of vaporization and sublimation.

In all of the molecules in Figure 1, the three bonds around each carbon are coplanar, as are those around each nitro nitrogen. For the bonds of the amino nitrogens, the situation is variable. They are coplanar in **6** and **7** and nearly so in **1** and **2**, in which the sums of the bond angles are

358°. In **3**, **8** and **9**, however, there is some pyramidal character; the sums of the bond angles are mostly between 346° and 350°, but as low as 331° in the amino group in **3** that is shown to be rotated away from the neighboring NH₂.

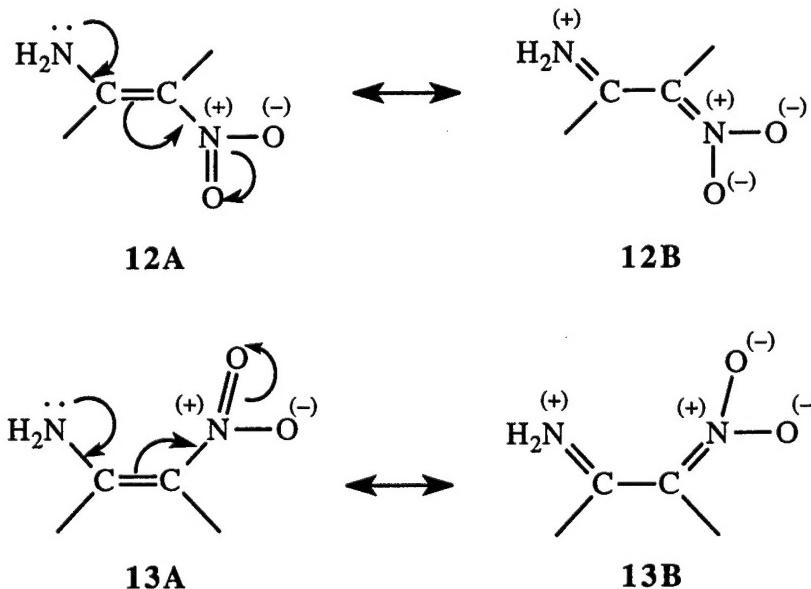
Apart from the pyramidal amino groups mentioned above, most of the molecules in Figure 1 are either exactly or nearly planar. The major exception to this is **3**, in which one NH₂ and one NO₂ are rotated significantly out of the approximate plane of the carbons and nitrogens, as depicted in Figure 1. The rotation of the NH₂ is probably in response to the opportunity to form three weak hydrogen bonds, while that of the NO₂ may be to minimize the interaction between the oxygens in the neighboring nitro groups.

4. Discussion

4.1 Relative Stabilities

In seeking to understand the relative stabilities within the groups **1 - 3** and **6 - 8** (Table 2), we shall focus upon two factors: (a) electron delocalization, and (b) intramolecular hydrogen bonding.

Electron delocalization in these molecules can involve the polarizable π electrons of the C=C double bond in conjunction with resonance donation by NH₂ enhanced by inductive withdrawal by NO₂. Two possibilities are shown below:



Structures **12B** and **13B** suggest that the extent of such “push-pull” delocalization can be gauged approximately by the shortening of the C–NH₂ and C–NO₂ bonds and the lengthening of the C=C. In order to permit such comparisons, Figure 1 includes the computed geometries of **9 - 11**, in which the combined effect is precluded.

We shall first consider **6 - 8**, which have only one substituent of each type. The geometries of **6** and **7** do reflect the delocalization shown in **12B** and **13B**. The C–NH₂ and C–NO₂ bonds are shorter than in **9** and **10** and the C=C is longer, the extents being slightly greater in **6** than in **7**. The coplanarity of the NH₂ bonds is also consistent with **12B** and **13B**. The structure of **8**, on the other hand, is incompatible with these types of delocalization.

Proceeding to **1 - 3**, all three of these can and do, at least to some degree, show the push-pull delocalization depicted in **12B** and **13B**. The calculated bond lengths indicate that the extent is greatest in **1**, followed by **2**. This is presumably because both **12B** and **13B** are relevant to **1** but only **13B** to **2**. Delocalization is least important in **3**, because it is disrupted for one NH₂,NO₂ pair by the rotations of these groups.

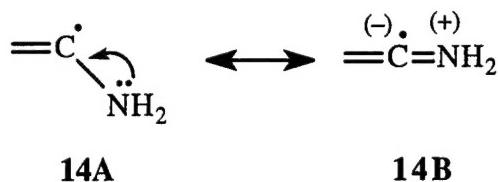
The possible hydrogen bonds (which are primarily of the type O···H) are shown in Figure 1 by dashed lines. There are two in **1**, and they can be considered to be relatively strong [14-16], with O···H distances R of 1.77 Å. There are four in **2**, but they are not as strong, with O···H separations of about 1.90 Å and 2.08 Å. **3** also has four hydrogen bonds, one being N···H in nature, but they involve considerably greater distances and hence are relatively weak. If it is assumed that hydrogen bonding can be treated roughly as a dipole-dipole interaction, so that $\Delta E \sim -1/R^3$ [17], then the stabilizing effect is greatest in **2**, by factors of about 1.4 over **1** and 2.2 over **3**. In the second group of molecules, **6 - 8**, if it is assumed that the hydrogens on the carbons are not involved, then there is hydrogen bonding only in **6** and **8** and its effect is greater in **6**.

In summary, consideration of electron delocalization alone predicts the relative stabilities to be **1 > 2 > 3** and **6 > 7 > 8**; these are the same trends as are in Table 2. Intramolecular hydrogen bonding is evidently a less significant factor, since it suggests that **2** should be more stable than **1** and **8** more than **7**.

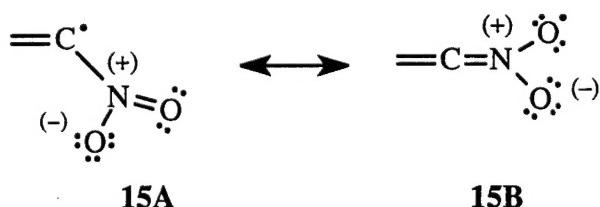
4.2 Dissociation Energies

In analyzing the computed C–NO₂ and C–NH₂ dissociation energies, Tables 3 and 4, it seems reasonable to take as reference points the respective methyl and ethyl derivatives, which have only one substituent and no π electrons. In these alkyl systems, the bond energies are approximately 60 kcal/mole for C–NO₂ (Table 3) and 85 kcal/mole for C–NH₂ (Table 4). The presence of the double bond, still with only one substituent, causes these values to increase to 70 kcal/mole (for **10**) and 103 kcal/mole (for **9**). This is consistent with the well-known observation that a single bond is shortened and strengthened by the presence of an adjacent multiple bond [19, 20]; for example, the C–H dissociation energy is about 10 kcal/mole higher in ethylene than in ethane [21]. Various interpretations of this have been offered [19, 20], including one based on evidence that a portion of the π charge extends into the neighboring bond region [22].

The introduction of the second substituent allows push-pull electron delocalization in **6** and **7**. It also permits intramolecular hydrogen bonding in **6** and **8**. These factors stabilize the undissociated molecules and thus further increase the C–NO₂ and C–NH₂ dissociation energies. The only exception to this is the C–NO₂ bond in **8**, which is actually weaker than in **10**. This is due to the unusual stability of the fragment formed from **8**, in which there is apparently some delocalization of the amino nitrogen lone pair, as shown in **14B**; this is reflected in a shortening of the C–NH₂ distance, from 1.370 Å in **8** to 1.355 Å in the fragment.



When all four substituents are present, then push-pull delocalization and intramolecular hydrogen bonding affect the stabilities of both the undissociated molecules and the fragments. In addition, some of the latter are stabilized by electron delocalization such as is depicted in **14B** and **15B**. It becomes difficult, therefore, to assess the relative effects of these various factors upon the dissociation energies. However the net result is that the latter are lower, in some instances, than in the doubly-substituted molecules; notable examples are the C–NO₂ bonds in **2** and **3**. In these cases, the fragments appear to be significantly influenced by structures analogous to **14B**; the C–NH₂ distances for the carbons that lose the NO₂ change from 1.350 Å and 1.397 Å in **2** and **3** to 1.314 Å and 1.328 Å, respectively. To illustrate the role of structures analogous to **15B**, the C–NO₂ distance for the carbon that loses the NH₂ in **2** decreases from 1.443 Å to 1.383 Å.



The strengths of the C–NO₂ bonds are of particular significance in the context of **1** - **3** as possibly-useful energetic molecules, since the ease of rupture of such bonds is one of the key determinants of the sensitivities of compounds to unintended external stimuli such as shock and impact [23-31]. It is very important to minimize this sensitivity. While it does not in general depend solely upon the C–NO₂ bond strength [31], the overall similarity of these molecules suggests that their sensitivities will increase from **1** to **2** to **3**.

4.3 Heats of Formation, Vaporization and Sublimation

For all three phases, the computed heats of formation of **1** - **3**, given in Table 5, follow the trend in molecular stabilities seen in Table 2 and discussed earlier. The heats of vaporization and sublimation, on the other hand, do not vary monotonically. We estimate these properties by means of formulas that relate them to the electrostatic potentials and the areas of the molecular surfaces [12, 13]. (The surface is taken to be the 0.001 au contour of the electronic density [32].) The areas increase slightly from **1** to **3**. However the total variance of the surface electrostatic potential, which is a measure of its spread or range of values [12, 13], is highest for **1**, decreases markedly for **2**, and then increases somewhat for **3**. This is the same pattern as is shown by the heats of vaporization and sublimation in Table 5. Thus the large values of these for **1** can be attributed to the strong negative potentials of the oxygens reinforcing each other at one end of the molecule, the positive potentials of the hydrogens doing the same at the other end, and the consequent relatively strongly- attractive intermolecular interactions.

The heat of formation is an important property of energetic compounds, since it helps to determine the amount of energy available for release upon chemical transformation. This is increased by a positive heat of formation; for example, the experimental values for RDX and HMX, **4** and **5**, are 16.9 and 17.9 kcal/mole, respectively [2]. In Table 6 are listed the heats of reaction for conversion to CO, N₂ and H₂O, for **1** - **3** and for RDX and HMX. While the process is exothermic in each instance, the heat release, on a molar basis, is roughly twice as great for RDX and HMX as for **1** - **3**; this is due in part to the heats of formation of the latter being negative. However, on a mass basis, which is what is important for energetic performance [1, 3], the differences are much less dramatic.

5. Summary

We have analyzed the structures and relative stabilities of the three isomeric diaminodinitroethylenes and the three isomeric aminonitroethylenes. The molecular geometries reflect the effects of two significant stabilizing factors: “push-pull” electronic delocalization and intramolecular hydrogen bonding. The first of these is sufficient to explain the relative stabilities within each group of molecules. The C–NO₂ and C–NH₂ bond dissociation energies reflect the roles of these factors in both the parent molecules and the fragments. In the latter, electronic delocalization involving the radical site can also be important. The gas, liquid and solid phase heats of formation of the diaminodinitroethylenes follow the trend in their molecular stabilities and are mostly negative or very weakly positive, consistent with the relative stabilities of these molecules. The decomposition of *cis*-diaminodinitroethylene to CO, N₂ and H₂O releases approximately 90% as much heat, on a mass basis, as do the corresponding processes for RDX and HMX.

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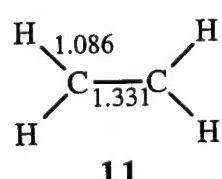
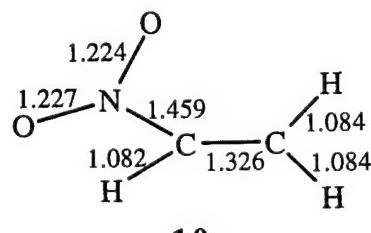
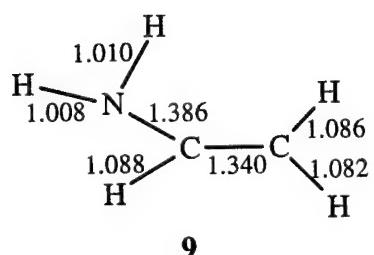
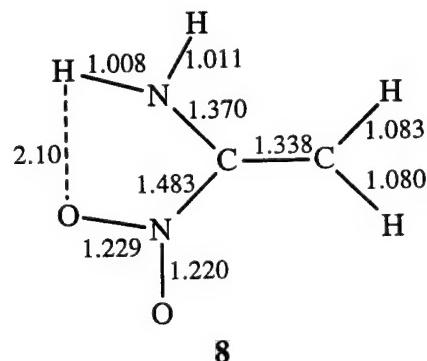
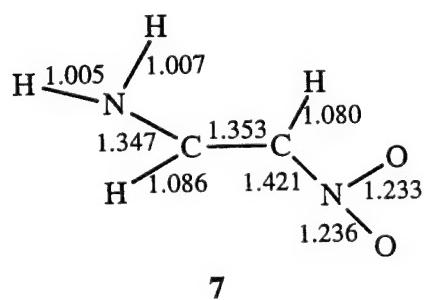
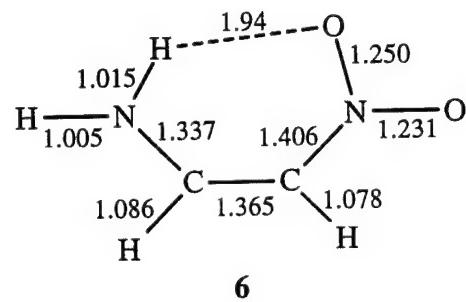
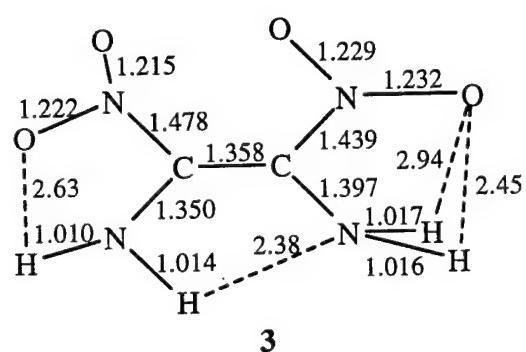
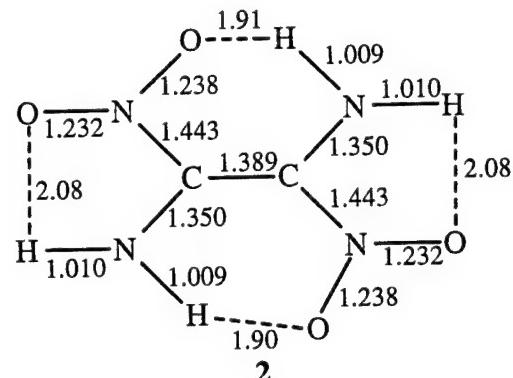
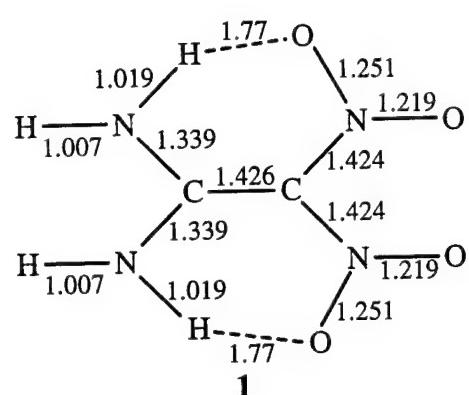
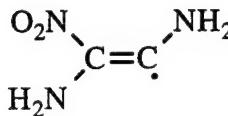
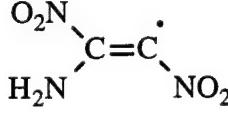
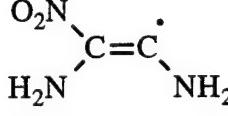
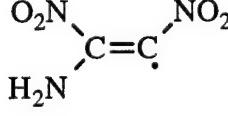
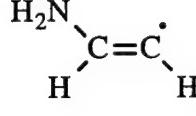


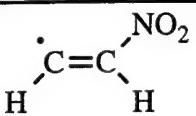
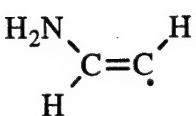
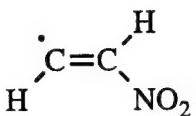
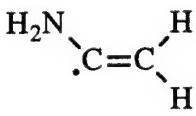
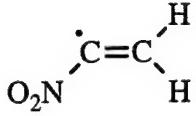
Figure 1. Optimized bond lengths, B3P86/6-31+G**.

Table 1. Computed energies, B3P86/6-31+G**.^a

System	E(0), hartrees	ZPE, kcal/mole	$\Delta H(0 \rightarrow 298)$, kcal/mole
<i>Undissociated molecules</i>			
1	-599.70979	58.23	64.58
2	-599.70209	57.59	64.08
3	-599.68278	58.07	64.80
6	-339.30953	46.20	50.34
7	-339.30220	45.76	50.21
8	-339.29272	45.28	49.58
9	-134.39501	43.37	46.45
10	-283.78047	34.68	38.22
11	-78.88388	32.09	34.59
<i>Dissociation products</i>			
(H ₂ N) ₂ C=•C(NO ₂)	-394.10862	48.24	53.40
(H ₂ N)•C=C(NO ₂) ₂	-543.48026	38.83	44.72
	-394.11362	48.52	53.43
	-543.47291	39.12	44.95
	-394.10438	48.22	53.29
	-543.45916	38.55	44.64
	-133.68460	34.71	37.82

(continued)

Table 1. Computed energies, B3P86/6-31+G** (continued).^a

System	E(0), hartrees	ZPE, kcal/mole	$\Delta H(0 \rightarrow 298)$, kcal/mole
	-283.06675	25.79	29.40
	-133.68258	34.76	37.87
	-283.06871	25.92	29.52
	-133.69595	34.67	37.90
	-283.06547	25.95	29.68
H ₂ C=CH·	-78.17703	23.03	25.57
NO ₂	-205.48464	5.65	8.08
NH ₂	-56.04295	12.00	14.38

^aE(0) is the energy minimum at 0 K; it does not include the zero-point energy (ZPE). $\Delta H(0 \rightarrow 298)$ is the enthalpy change in going from 0 K to 298 K; it includes the ZPE. Since E(0) = H(0), it follows that H(298) = E(0) + $\Delta H(0 \rightarrow 298)$.

Table 2. Relative stabilities, B3P86/6-31+G**, within the groups **1 - 3** and **6 - 8**.

Molecule	Relative enthalpy at 298 K, kcal/mole
3	17.2
2	4.3
1	0
<hr/>	
8	9.8
7	4.5
6	0

Table 3. Calculated C–NO₂ dissociation energies, B3P86/6-31+G**

Dissociation process	$\Delta H(298)$, kcal/mole		
(H ₂ N) ₂ C=C(NO ₂) ₂ → (H ₂ N) ₂ C=·C(NO ₂) + NO ₂	70.0		
1			
O ₂ N H ₂ N C=C NH ₂ NO ₂	→	O ₂ N H ₂ N C=C NH ₂ + NO ₂	62.6
2			
O ₂ N H ₂ N C=C NH ₂ NO ₂	→	O ₂ N H ₂ N C=C NH ₂ + NO ₂	55.4
3			
H ₂ N C=C H NO ₂	→	H ₂ N C=C H H + NO ₂	83.6
6			
H ₂ N C=C H NO ₂	→	H ₂ N C=C H H + NO ₂	80.4
7			
H ₂ N C=C H O ₂ N H	→	H ₂ N C=C H H + NO ₂	66.8
8			
O ₂ N C=C H H	→	·C=C H H + NO ₂	70.0
10			
H ₃ C–CH ₂ NO ₂ → H ₃ C–·CH ₂ + NO ₂	(60) ^a		
H ₃ C–NO ₂ → H ₃ C· + NO ₂	59.8 (60.6) ^a		

^aExperimental values, in parentheses, were obtained from ref. 18.

Table 4. Calculated C-NH₂ dissociation energies, B3P86/6-31+G**.

Dissociation process	$\Delta H(298)$, kcal/mole
$(\text{H}_2\text{N})_2\text{C}=\text{C}(\text{NO}_2)_2 \longrightarrow (\text{H}_2\text{N})\dot{\text{C}}=\text{C}(\text{NO}_2)_2 + \text{NH}_2$	111.6
1	
$\begin{array}{c} \text{O}_2\text{N} \\ \\ \text{H}_2\text{N}-\text{C}=\text{C}-\text{NH}_2 \\ \quad \backslash \\ \text{NO}_2 \end{array} \longrightarrow \begin{array}{c} \text{O}_2\text{N} \\ \\ \text{H}_2\text{N}-\text{C}=\dot{\text{C}}-\text{NH}_2 \\ \quad \backslash \\ \text{NO}_2 \end{array} + \text{NH}_2$	112.1
2	
$\begin{array}{c} \text{O}_2\text{N} \\ \\ \text{H}_2\text{N}-\text{C}=\text{C}-\text{NO}_2 \\ \quad \backslash \\ \text{NH}_2 \end{array} \longrightarrow \begin{array}{c} \text{O}_2\text{N} \\ \\ \text{H}_2\text{N}-\text{C}=\dot{\text{C}}-\text{NO}_2 \\ \quad \backslash \\ \text{NH}_2 \end{array} + \text{NH}_2$	107.6
3	
$\begin{array}{c} \text{H}_2\text{N} \\ \\ \text{H}-\text{C}=\text{C}-\text{NO}_2 \\ \quad \backslash \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \cdot \\ \text{H}-\text{C}=\dot{\text{C}}-\text{NO}_2 \\ \quad \backslash \\ \text{H} \end{array} + \text{NH}_2$	118.8
6	
$\begin{array}{c} \text{H}_2\text{N} \\ \\ \text{H}-\text{C}=\text{C}-\text{H} \\ \quad \backslash \\ \text{NO}_2 \end{array} \longrightarrow \begin{array}{c} \cdot \\ \text{H}-\text{C}=\dot{\text{C}}-\text{H} \\ \quad \backslash \\ \text{NO}_2 \end{array} + \text{NH}_2$	113.3
7	
$\begin{array}{c} \text{H}_2\text{N} \\ \\ \text{O}_2\text{N}-\text{C}=\text{C}-\text{H} \\ \quad \backslash \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \cdot \\ \text{O}_2\text{N}-\text{C}=\dot{\text{C}}-\text{H} \\ \quad \backslash \\ \text{H} \end{array} + \text{NH}_2$	110.1
8	
$\begin{array}{c} \text{H}_2\text{N} \\ \\ \text{H}-\text{C}=\text{C}-\text{H} \\ \quad \backslash \\ \text{H} \end{array} \longrightarrow \begin{array}{c} \cdot \\ \text{H}-\text{C}=\dot{\text{C}}-\text{H} \\ \quad \backslash \\ \text{H} \end{array} + \text{NH}_2$	103.3 (102) ^a
9	
$\text{H}_3\text{C}-\text{CH}_2\text{NH}_2 \longrightarrow \text{H}_3\text{C}-\dot{\text{C}}\text{H}_2 + \text{NH}_2$	(84) ^a
$\text{H}_3\text{C}-\text{NH}_2 \longrightarrow \text{H}_3\text{C}\cdot + \text{NH}_2$	84.6 (85.4) ^a

^aExperimental values, in parentheses, were obtained from ref. 18.

Table 5. Calculated heats of formation, vaporization and sublimination of compounds **1** - **3**, in kcal/mole.

Compound	Heat of formation, 298 K			Heat of vaporization	Heat of sublimation
	gas	liquid	solid		
1	-1	-16	-27	15	26
2	1	-11	-19	12	19
3	15	2	-7	13	22

Table 6. Heats of reaction for conversion to CO, N₂ and H₂O.^a

Compound (solid state)	ΔH (kcal/mole)	ΔH (cal/g)
1	-141	-954
2	-150	-1012
3	-162	-1093
RDX	-270	-1214
HMX	-355	-1198

^aThese results were obtained using the calculated heats of formation for **1 - 3** (Table 5) and experimental values for RDX and HMX (ref. 2) and for CO and H₂O (ref. 18).